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INVESTIGATION OF LITHIUM SULFUR DIOXIDE (Li/SO₂) BATTERY SAFETY HAZARD

Quarterly Report for the Period December 24, 1980 - March 23, 1981

Contract No. N60921-81-C-0084

Prepared by

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Prepared for
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Silver Spring-White Oak
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ABSTRACT

The Li/SO_2 primary electrochemical cell has received considerable attention as a high energy power source in the last decade. However, during the same time a number of safety hazards have been associated with its use. This report is the initial part of a research-oriented investigation intended to identify and document present Li/SO_2 safety hazards, then to identify the chemical reactions responsible for these hazards, and finally to investigate methods of controlling them.

This report presents the results of a survey of the safety hazards associated with Li/SO₂ cells. The report documents specific safety incidents experienced with Li/SO₂ cells, presents some of the causes identified or postulated for the incidents, and identifies general aspects of Li/SO₂ use presently believed to be potentially hazardous.

The survey was carried out by reviewing safety studies and reports of safety incidents appearing in the literature and by gathering unpublished information of the experiences of users of Li/SO₂ cells in both government and industry. The results of the report can serve as basis for deciding which aspects of the Li/SO₂ safety hazard at present need further investigation. \

Acknowledgement

We acknowledge the helpful suggestions of Dr. S. D. James, NSWC Contract Monitor in the preparation of this report.

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1. INTRODUCTION

The Li/SO₂ cell has outstanding features including high specific energy, high volumetric energy density, long shelf life, extremely stable voltage and outstanding low temperature performance (1-10). These characteristics make the Li/SO₂ system desirable for use in a wide range of areas including military, industrial and consumer applications. The active cell materials which provide for these desirable characteristics are also responsible for a complex cell chemistry which, under certain conditions, results in a thermodynamically unstable system and thus a complex safety issue (11-12). As the use of Li/SO₂ cells increase the concern over the related safety problems will also increase until they can be eliminated or controlled.

Because of the complexity of the Li/SO₂ cell chemistry, the actual causes of many of the reported safety incidents are not well understood. It is the purpose of this program to investigate the various safety hazards and find solutions to them. In this report we present a literature and user survey on the safety aspects of Li/SO₂ cells.

2. THE BACKGROUND OF THE Li/SO₂ CELL

2.1 Cell Design and Normal Discharge

A typical Li/SO₂ cell contains a Li anode and a porous Teflon bonded carbon cathode on an Al current collector. Sulfur dioxide serves as the depolarizer. The typical electrolyte consists of sulfur dioxide (~70 w/o), acetonitrile and LiBr (1-2 molal). A fresh cell has an internal pressure of 3-4 atmospheres at 20°C, thus the cells are designed to contain high pressures without leakage and to safely vent if the internal pressure exceeds a specific value.

Lithium is thermodynamically unstable in the presence of acetonitrile and reacts exothermically, forming methane gas and other products (12-15). However, in the presence of SO₂ the surface of the Li anode is passivated, presumably by the formation of a layer of Li₂S₂O₄, providing a kinetic stability to the system (10,12).

The overall reaction in the Li/SO₂ cell is believed to be



The discharge product, Li₂S₂O₄, is insoluble and precipitates within the porous carbon cathode (8,10,16).

Lithium dithionite is believed to be the sole cathode product formed upon discharge to 1.5V, however, attempts to quantitatively determine it have given less than theoretical amounts (12). This suggests the likely formation of other sulfur oxy compounds. Because of the susceptibility of dithionite to decompose during analysis to form other sulfur-oxy compounds, quantitative determination of dithionite poses a major problem. As mentioned, the major components in the Li/SO₂ cell are Li, SO₂, CH₃CN and C. A complex relationship exists among these four components which determine the inherent safety of the Li/SO₂ system during storage, use and abuse.

Three different types of cells, Li limited, SO₂ limited or cathode limited, can be designed by varying the relative amounts of Li, SO₂ or cathode. All three types have been examined to various limits (16-21) in regards to safety and efficiency of performance.

The SO₂ limited cell is reported to be the most unsafe and undesirable configuration. At the end of normal discharge (SO₂ depletion) the excess lithium is completely unprotected and reacts with the acetonitrile yielding methane, LiCN and reportedly numerous other compounds. This reaction reportedly results in a violent venting of the cell (16-18).

In cathode limited cells the end of normal discharge occurs when the porous carbon cathode is choked by the buildup of $\text{Li}_2\text{S}_2\text{O}_4$. Under these conditions the remaining Li can still be passivated by the excess SO_2 (15,18). The cells are apparently more safe.

The third option is the lithium limited cell (17,19). At the end of discharge there is no lithium left, thus the reaction between Li and acetonitrile is not possible.

Current commercial Li/ SO_2 cells employ one of the latter two designs; the choice being made on the basis of the rate/capacity requirements of the cells. Usually Li limited cells are capable of higher capacities at higher rates, but at low rates due to the limited amount of Li they are less efficient than cathode limited cells.

Even though a cell is claimed to be of one design under specific discharge conditions, in practice it may not be true. For instance at low discharge rates a cell designed as cathode limited may actually be lithium limited, while a cell designed as lithium limited may be cathode limited at high discharge rates. Often such differences also arise from quality control problems.

2.2 Overdischarge

Less is known about the processes which occur in abusive discharge modes. The forced overdischarge situation maybe encountered by a weak cell in a battery package. At the end of the normal discharge, the cell voltage rapidly drops towards and on forced overdischarge below zero volts.

A number of reactions can occur during forced overdischarge of a Li/ SO_2 cell. In a SO_2 limited or a cathode limited cell the major reaction at the cathode is believed to be (18)



This reaction results in Li being deposited on the carbon cathode. The plated Li could then react with the acetonitrile or other materials present in the cell.

At the anode of these cells, the main reaction during voltage reversal is the electrostripping of Li until the Li is depleted or becomes separated from the anode current collector (18,21). After this point, the anode potential could rise to positive values leading to oxidation of the electrolyte or other materials. Oxidation of the electrolyte could result in many species, some potentially hazardous; however, there is little work reported in this area.

At the end of normal discharge of a Li limited cell, on the other hand, the anode potential rises to positive values and the major reactions would be oxidation of the electrolyte, SO_2 or discharge products. The cathode potential would maintain its relatively high positive values until at least all the SO_2 is depleted.

The chemistry and electrochemistry in Li/ SO_2 cells during forced overdischarge are clearly dependent on the conditions which limit their normal discharge.

2.3 Nature of Safety Studies

Two major approaches for the investigation of the safety of Li/ SO_2 cells involve: (i) thermal studies; and (ii) chemical studies. There has been a number of reported thermal studies (12, 19, 22-26) however, few chemical studies have been carried out (12, 16, 18, 27, 28).

Based on DTA studies of cell materials, components and actual Li/ SO_2 cells, Dey concluded (24) that the major reactions which contribute to the thermal runaway of the cells are the reaction of Li and acetonitrile, the decomposition of $\text{Li}_2\text{S}_2\text{O}_4$ and the reaction of Li and sulfur (from the decomposition of $\text{Li}_2\text{S}_2\text{O}_4$). Other thermal studies have been in general agreement with the results. A major deficiency with these studies is the lack of product identification.

The small number of reported chemical studies on the safety of the Li/ SO_2 cell are qualitative in nature. Some of the numerous compounds reported to have been found in Li/ SO_2 cells are listed in Table 1. In many cases the products were identified from cells which had vented, or exploded or after exposure of the cells to the atmosphere. Thus it cannot be ascertained whether all the compounds identified actually formed in the cell prior to the incident or whether they formed during or after the incident, or from exposure to the atmosphere. Decomposition during the analytical procedures is also of concern.

In one quantitative study Taylor (18) reported data on cyanide formation in overdischarged Li/ SO_2 cells which he attributed to the reaction of Li (or LiAl) and acetonitrile. The amount of cyanide in the cells was shown to depend on the amount of time the cell was allowed to stand before the analysis. No data was reported on partially discharged cells.

TABLE 1
LIST OF CHEMICALS FOUND IN Li/SO₂ CELLS

<u>Starting Materials</u>	<u>Chemicals Generated</u>
Li, SO ₂ , C, Teflon, Propylene carbonate, Ni, Al, Stainless steel, Acetonitrile, LiBr, Polypropylene.	Li ₂ S ₂ O ₄ , Li ₂ S ₂ O ₃ , S ₂ Br ₂ , SOBr ₂ , H ₂ , Br ₂ , S, CS ₂ , H ₂ S, CH ₄ , C ₂ H ₆ , C ₂ H ₄ , LiOH, Li ₂ O, Li ₃ N, Li ₂ CO ₃ , LiCN, Dimethylquinoline, 4-amino-2-,6-dimethylpyrimidine, 2-amino-5-phenylpyrazine, 6-phenyl-2-pyridone.

4. Li/SO₂ CELL SAFETY

A survey of many users of Li/SO₂ cells and a review of literature have revealed a number of concerns over the potential safety hazards of Li/SO₂ cells. A prior survey on the safety of Li/SO₂ cells appeared in 1977 (11). Clearly, there are many incidents which have never been reported, especially cases experienced by persons who were using cells in safety tests or evaluating them for specific uses. From our survey of users it appears that anyone who has worked with Li/SO₂ cells for an extended period of time has encountered some type of safety incident ranging from minor leakage of SO₂ to explosion of a cell.

Incidents involving venting due to shorting, especially when brought about intentionally, do not fall under the definition of a safety hazard, since the performances of the cells are as expected under the conditions of operation. However, some related incidents are reported here since they occurred unintentionally during use.

Summarized below are incidents reported in the literature or related by users of Li/SO₂ cells along with some general conditions that investigators have identified as having a high probability of causing cells to vent or explode. Some of the possible causes for these incidents are discussed in the following section.

3.1 Safety Hazards Reported in the Literature

The early users of lithium cells encountered safety problems which have continued up to the present. In 1972, Wilburn (1) reported that lithium batteries might be unsafe under some conditions. He found that when Li/SO₂ cells were short circuited, the internal pressure and temperature increased to a point where the cells ruptured and caught on fire. By 1974 several investigations had been started to determine the causes of the safety incidents encountered by potential users of Li/SO₂ cells and batteries. References 2 and 5 report the results of two of these investigations. Brooks (5) devised seven tests for cells, (a) short circuit, (b) increasing load, (c) hot plate, (d) cell deformation, (e) dynamic environment, (f) case rupture, (g) incineration, and five tests for batteries, (a) short circuit, (b) increasing load, (c) hot plate, (d) fresh and salt water immersion, (e) reverse discharge. All cells in his experiments contained vents and all batteries contained 10 ampere fuses. Cells and batteries malfunctioned, i.e., vented or fuse opened, on all of his tests with the exception of the case rupture and the water immersion. There was some loss of capacity in the samples discharged after the water immersion tests. Warburton (2) found during the discharge of "C" size cells at approximately the 30 minute rate that the internal cell temperature rose to approximately the melting point of lithium (180°C) and those with vents vented and those without vents exploded. He estimated that the internal pressure of the test cells reached 30 atmospheres.

Taylor and MacDonald of the P. R. Mallory Company (20) abuse-tested Mallory D-cells with 500 cm² cathodes and vents designed to open at 450 ±40 psia. In one set of tests, cells were incinerated at 520°C for 20 minutes. They quietly vented. On short-circuit, there were differences between fresh cells and stored cells. Fresh cells were tested at room temperature and at 72°C (insulated) in various states of charge. The initial short circuit current was ~70A, and this fell to ~55A after a few seconds. The cell(s) quietly vented and, in one instance, a maximum wall temperature of 83°C was reported. Cells stored for one month at 72°C showed lower short circuit currents and did not vent unless they had been previously partially discharged at -30 or -40°C.

The one abuse-mode for which an explosion was reported (20) was when charging a fully discharged cell. It was asserted that "experience.... (in this area was) not extensive." A fully charged ~10 Ah nominal capacity cell was charged for 10.5 Ah at 0.5A. There were no untoward events. The cell was then discharged. Discharge was normal, although somewhat shorter than usual. This was ascribed to electrical isolation of as-plated Li due to reaction with the solvent, as is frequently observed. In a subsequent test, a cell stored at room temperature for 130 days was discharged to -0.8V at 0.5A and then charged at 0.5A. The voltage rose sharply to 3.16V and, over 20 hr, to 3.4V. During the next hour the temperature and pressure rose and the terminal potential rose to 3.5V. Suddenly, the temperature started to increase and, to quote, "The cell vented with explosive violence at a wall temperature >>280°C."

DiMasi (16) reported that in a field test in August 1975, of 24V batteries, there were instances of overheating at low or moderate discharge rates and some cells exploded. The explosions were observed at or near rated capacity at the point where the poorer cells were driven into reversal. It was shown that this is a particular problem with cells limited by the amount of SO₂ in the system rather than by blockage of the carbon cathode, as is usual. It was suggested that in an SO₂-limited cell, excess Li is no longer filmed and is free to react with AN. It was suggested that excessive pressure could result from the previously discussed reaction of Li with AN, to form CH₄.

Recently, Dey has reported (19) on the effect of cell design variables such as stoichiometric ratios of Li:SO₂ electrode area, SO₂ content of the electrolyte, etc., on the explosion hazard of hermetic Li/SO₂ D-cells on forced overdischarge. Explosions were observed under some conditions and the Li:SO₂ ratio was identified as an important parameter affecting the safety of the cell. Dey concluded that the Li-limited cell designs were safer than the Li-rich cell designs.

3.2 Safety Related Experiences of Li/SO₂ Cell Users

A number of accidents occurred in aircraft equipments resulting in a ban on the use of Li/SO₂ cells on aircrafts. Most of the cells were used to power Emergency Locator Transmitter (ELTs). A few of the accidents, as described in Reference 11, are listed below.

(i) A fire on an aircraft life raft, while in a warehouse in Miami, resulted from the batteries in the ELT (11).

(ii) A fire in a Cessna 182 while in flight was blamed on the Li/SO₂ batteries in the ELT carried on the plane (11).

(iii) An explosion which occurred on board a Bonanza while in a hanger in Chicago was attributed to the Li/SO₂ batteries in the on-board ELT (11).

(iv) During an inspection of emergency equipment on a Northwest Airlines aircraft a fire occurred and was blamed on the Li/SO₂ batteries in the ELT (11).

(v) A Li/SO₂ battery exploded on board a Delta Airlines Lockheed L1011 aircraft after it had been used for three hours to power a light during a test of the slide raft equipment (11).

No reasons for the venting or explosion of the Li/SO₂ cells in these incidents were given with the report of these cases. However, the cells were of the crimped seal design which was banned by the FAA.

(vi) The Air Force has reported explosions of Li/SO₂ batteries used as energy sources for SDU-30/E distress lights in life survival kits. The batteries (K316LI) consist of 4 "D" size cells encased in a butyrate case. The cause of the explosion was attributed to expansion of the SO₂ under pressure and the resultant rupture of the case. The expansion of the SO₂ resulted from exposure to high heat conditions encountered in normal aircraft operations (29).

(vii) The extent of the safety hazard associated with the use of Li/SO₂ cells in aircraft is shown in this report in The Christian Science Monitor, March 8, 1979 (30).

"Batteries that power emergency radio transmitters in 60,000 or more planes - one-third of the U.S. air fleet - must be removed promptly because they may explode or burst into flames, according to Federal Aviation Administration (FAA). An agency spokesman said a mandatory "Airworthiness Directive" ordering the removal of all Lithium Sulphur Dioxide (Li/SO₂) batteries was sent to owners of U.S.-registered aircraft because of a rash of incidents involving exploding batteries in the past six months.

In 1979 the FAA (31) required removal of all Li/SO₂ cells from U.S. aircraft until new safety guidelines were established.

The following incidents occurred during testing of Li/SO₂ cells.

(viii) Tests of Li/SO₂ cells at NASA Langley (32) showed that under certain conditions the cells would reproducibly explode and burn. The conditions were described as follows. Twelve cells (Mallory L026HS, 6.4 Ah rated capacity) were forced discharged at 2A at -35°C for 4.8 hours. At the end of discharge the cells were approximately one volt into reversal. All twelve cells exploded within 20 to 30 minutes after being removed from the test. The cause was reported as unknown. All the cells apparently had warmed up to room temperature prior to the incident.

(ix) In a similar test at NASA Langley (11) D-size Li/SO₂ cells were forced discharged at 2A and -20°C. At the end of the discharge the cell voltage was approximately -0.4 volts except for a -1 volt spike which occurred shortly after voltage reversal. Within 16 to 30 minutes of removing the cells from the test they exploded. It was noted that cells removed from the test prior to the -1 volt spike became warm but did not explode or vent.

Dr. R. F. Bis of NSWC (33) has found that Li/SO₂ batteries and cells that have been stored after partial discharge are reproducibly more dangerous when subjected to abusive treatment than fresh cells. Two dangerous conditions he has identified are described below.

(x) Single cells which were stored after partial discharge were found to react more violently than fresh cells when incinerated or discharged into reversal.

(xi) Dr. Bis also reported the violent venting of 27V batteries, consisting of 36-D cells arranged in four parallel strips of nine cells in series, after being subjected to the following sequence of events:

- 1) the batteries are discharged by as little as 20% then,
- 2) ambient storage for 3-4 months then,
- 3) 3 or 4, one second shorts followed by open circuit.

Within five minutes the batteries, still on open circuit, vent violently.

A few reported safety incidents have involved discharged Li/SO₂ cells which appear to be shock sensitive. In all cases reported, the cause of the incident was not known and it could usually not be reproduced.

(xii) The Honeywell Power Sources Center reported (27,34) that a discharged Li/SO₂ cell exploded while being prepared for post mortem analysis. The explosion occurred while the cell container was being punctured.

It was noted that the cell had been exposed to the atmosphere before the accident. Other cells with similar histories were also reported to explode when dropped from a height of five meters.

(xiii) During a five year testing program at Sandia, two safety incidents occurred with Li/SO₂ D-size cells (35). The first incident occurred with a cell that had been discharged at 200 μ A with the following temperature cycle: -18°C for two months, +20°C for two months, +49°C for two months, -40°C for one day, and +70°C for one day. After six months the cell was discharged through a 10 Ω load at 20°C to <2 volts. The cell spontaneously vented with flame while being removed from the wooden test rack after the test. Four other cells subjected to the identical test did not vent.

(xiv) The second incident at Sandia occurred with a cell that was stored on open circuit at 35°C for 1-1/2 years. At the end of the storage period the cell was discharged through a 10 Ω load at 20°C to <2 volts. The cell was accidentally dropped on the floor after the test and vented with flame. This behavior could not be reproduced with four other cells subjected to the same test.

Both of the safety incidents at Sandia involved cells with a Li/SO₂ ratio of 1.5.

(xv) The shock sensitivity of Li/SO₂ cells was again demonstrated in a report (11) that stated that three of 11 cells that were discharged (apparently at -54°C) exploded when dropped onto concrete from a height of 16 feet. No further details were given.

The following incidents are believed to have occurred because of mechanical failure of the cells during testing.

(xvi) An explosion in a series stack of 12, 1/2C size Li/SO₂ cells occurred at Harry Diamond Labs while being used in a military communication equipment (36). The battery exploded approximately 20 seconds after initiating the discharge at a one hour rate. Prior to the discharge the battery was subjected to an 8000 g shock test. The OCV of the battery after the shock test was lower than expected approximately by the voltage of one cell in the stack. The cells were potted in hard epoxy in a steel case, however, it is believed that a blocked vent was not responsible for the explosion. The accident was not reproducible.

(xvii) Two Li/SO₂ battery packs vented with flame while undergoing sinusoidal vibration testing at NASA (37). The failures were reported to have resulted from internal cell shorting, external cell shorting (positive lead to battery case) and the opening of internal conductors in individual cells.

The causes of the following two incidents are not known. However, it is very possible that at least one cell in each battery was bad and was forced into voltage reversal.

(xviii) At the Brunswick Corporation in Costa Mesa, California (38), an 11 cell Li/SO₂ battery vented and burst into flames during a load test. The battery consisted of 11 C-size cells and was being discharged across a load of 12.8 Ω which was drawing approximately 2.5 amperes. During most of the 2-1/2 hours of discharge the battery voltage was 28 volts. After the voltage fell to 17 volts (1.5V/cell) it was noted that both the voltage and temperature began to increase. This resulted in the battery venting with flame. This behavior could not be reproduced in similar tests.

(xix) An explosion of a Li/SO₂ battery was reported at the Hazeltine Laboratory in Braintree, Massachusetts, while being tested in a Target MK38 (11). The battery consisted of 13 Li/SO₂ cells and was discharged at approximately the one hour rate. The test was ended when the battery voltage reached 24 volts (1.85V/cell). Shortly after the discharge was terminated the battery exploded and caught fire.

(xx) G. J. DiMasi of U.S. Army ET and D Laboratory, Fort Monmouth, NJ, has recently presented results on his studies of the safety of Li/SO₂ cells at the NASA Workshop (39). He showed that low temperature forced overdischarge could lead to explosion or venting - the cell pops, fumes, and occasionally catches fire. The key variables were identified as Li/SO₂ ratio and discharge rates. At higher current densities, the SO₂ in the cell is not used efficiently; and the cells become carbon limited. Li plates onto the carbon during overdischarge. The plated Li, which has a surface area 100-200X that of Li foil, reacts with CH₃CN. Depending on the amount of Li, the reaction can become violent. He thinks that the reaction between Li and CH₃CN is autocatalytic and can be initiated by resistive heating. If sufficient Li is present, a thermal runaway reaction results.

Four accidents involving a BA5590 Li/SO₂ battery have occurred during five years of use by the Army (40). The battery consists of 10, 8 Ah cells in series. The four incidents are summarized below.

(xxi) Two incidents (Fort Mead and Fort Brag) involved the venting of a cell(s) in a battery pack containing two BA5590 batteries in parallel with no diode protection. The battery was being used as a constant power source in a radio with both receiving and transmitting capabilities. The batteries received almost constant use and were discharged to ~15V (1.5V/cell). The venting of a cell(s) in both cases is believed to have resulted from the forced overdischarge of a weak cell(s) in the batteries.

(xxii) A third incident at Fort Sill involved a BA5590 Li/SO₂ battery while it was being used as a power supply for a switching device. The current drain was 90 mA. One cell in the battery vented after ~1 hour of discharge. All the other cells were found to be normal and the cause could not be identified.

(xxiii) The fourth incident occurring at Fort Huachuca involved the venting of a cell(s) in another BA5590 battery used to power a location transmitter. The battery was near the end of its life when the failure occurred. The current is believed to have been higher than normal through at least part of the discharge. The cause of the accident has not yet been identified.

Two safety incidents reported by Sonatec in Goletta, California (41) involving communication equipments, are described below.

(xxiv) The first incident involved the rupture of a Li/SO₂ battery housing following the venting of the cells inside. The battery consisted of ~56 D-size (9 Ah) Li/SO₂ cells arranged in several parallel strings. The current was in the μ A range when the equipment was in the receiving mode and ~1A during transmission. The maximum current was within the rated limits of the individual cells. The battery incident is believed to have resulted from the shorting of the battery to the housing wall which was at ground potential. The shorting probably occurred because of failure or improper installation of insulation around the battery.

(xxv) The second incident involved the same type of battery and equipment and is still under investigation.

(xxvi) An accident known as the "Bermuda Incident" involved the explosion of a Li/SO₂ battery containing two separate stacks of 36 D-size cells connected in series. Further information from persons knowledgeable about the "incident" can not be reported because of pending court cases arising from the accident.

3.3 Summary of Li/SO₂ Cell Accidents

Most Li/SO₂ accidents can be grouped into one of the following five categories according to the type of use or abuse which resulted in the accident:

- a) overdischarge
- b) low temperature discharge
- c) charging
- d) storage after partial discharge
- e) shorting of cells

Based on these categories the incidents reported above can be arranged as shown in Table 2. The incidents listed under "other" resulted from unknown causes.

a) Overdischarge of Li/SO₂ cells can be further divided into one of two types - the first being discharge to less than 2V but more than 0V and the second - forced overdischarge to below 0V. It has been suggested that the discharge reactions which occur between 2 and 0V are different than the above 2V but the processes have not been extensively investigated. When a single cell is used as a power supply, discharge to below 0V will not occur, however, in a battery it is very possible that a weak cell(s) will be driven into voltage reversal unless prevented by the proper selection and placement of diodes.

The main hazard associated with overdischarge appears to be the formation of a potentially explosive compound or mixture of compounds within a cell during overdischarge. Since overdischarge is the most common cause of failure of the Li/SO₂ system further study of the phenomenon is warranted.

b) The major problem associated with low temperature discharge, particularly overdischarge, appears to be related to the energetic reaction between Li and CH₃CN which, while inhibited at low temperatures, is rapidly initiated as the cell is warmed to room temperature. This hazard mode appears most dangerous when a weak cell(s) in a battery is forced into voltage reversal during a low temperature discharge.

If this hazard mode is as reproducible as reported in safety incidents viii and ix it deserves extensive investigation.

c) Charging of a Li/SO₂ cell is another hazard mode which is likely to result in cell venting. The reactions that occur within a cell during charging will differ depending on the previous history of the cell, i.e., overdischarged, discharged, fresh, etc. However, with a minimum amount of care this hazard mode is easily avoided as evidenced by the absence of reported incidents.

d) Storage of partially discharged Li/SO₂ cells and batteries has been shown to increase the susceptibility of the Li/SO₂ system to abuse hazards. The abuse modes which have been examined in this situation include shorts, high pulses, overdischarge or incineration.

This hazard mode may be the most dangerous since in actual use many cells and batteries can be expected to experience use-storage cycles. If at the same time, they are inadvertently abused it is possible that many of them will vent violently. Further investigation of this problem is needed.

TABLE 2
SUMMARY OF Li/SO₂ CELL SAFETY PROBLEMS

<u>Hazard Mode</u>	<u>Incidents</u>	<u>Number of Incidents</u>
Overdischarge	xiii, xiv, xviii, xix, xxi	5
Low temperature discharge	viii, ix, xv, xx	3
Charging		0
Partial discharge-storage	x,xi	2
Shorts	xvii, xxiv, xxv	3
Other	xii, xvi, xxii, xxiii, xxvi	5

e) The venting of cells, particularly in a battery, due to shorts or high rate discharges can cause serious safety problems; however, most if not all of these hazards can be eliminated by the proper selection and placement of fuses, diodes, thermal switches (or fuses) insulation, and packing in the battery packs.

3.4 Causes of Safety Hazards in Li/SO₂ Cells

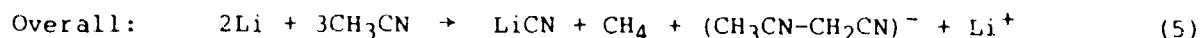
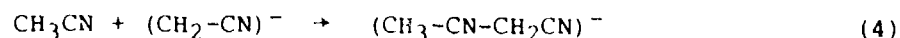
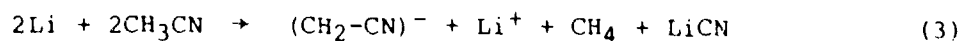
It is generally agreed upon that many of the internal cell components combust rapidly at high temperatures. Many of the safety incidents suggest that the venting or explosion could have been initiated by localized heating, spark, mechanical shock or an uncontrolled reaction between lithium and acetonitrile.

The most commonly cited reason for the safety incidents, particularly during voltage reversal, is the reaction of Li with acetonitrile. A major product of the reaction is methane. There are a number of ideas of the reaction mechanism. The simplest explanation for the formation of methane is that the fresh deposited Li during cell reversal has a surface area of 100 to 200 times that of the Li anode and is not completely passivated by the remaining SO₂. Therefore, the Li is unprotected and reacts with the acetonitrile.

It was also reported by Taylor (18) that the plated Li reacts with the Al current collector of the cathode forming Li/Al alloy. Taylor reported that Li/Al alloy is much more reactive with acetonitrile than Li and that the formation of Li/Al alloy in the cell leads to the production of methane. However, other studies suggest that (22) Li/Al alloy is less reactive than pure Li. In either case the presence of Li/Al in a discharged cell has not been confirmed.

Another possibility is that the plated Li reacts with the carbon forming Li intercalates which are suspected to be very reactive with acetonitrile (42-45). The formation of Li intercalates of graphite has been suggested from cell data, however, its actual presence has not been confirmed in discharged cells.

It is very possible that in actual cells all three situations occur under the proper conditions. Whatever state the plated Li is in, it is certain that its reaction with acetonitrile results in the formation of methane and/or other combustible materials. One reaction mechanism postulated for the formation of methane, LiCN and β-imino-n-butyronitrile is (17),



Other products such as C₂H₆ have also been claimed in forced overdischarged cells (18).

If the reaction between lithium and acetonitrile is rapid and sufficient materials are available, enough heat can be generated to initiate a thermal runaway reaction within the cell. Thermal studies (22,24,26) have shown that the decomposition of $\text{Li}_2\text{S}_2\text{O}_4$ to S, SO_2 and probably Li_2SO_3 occurs at $\sim 180^\circ\text{C}$ with the release of a substantial amount of heat. Once the $\text{Li}_2\text{S}_2\text{O}_4$ decomposes, any lithium left in the cell will react with the sulfur releasing additional energy. Thus if enough heat is generated by the reaction of lithium and acetonitrile other uncontrolled exothermic reactions will occur within the cell. The end result is a rapid increase in the temperature and pressure within the cell resulting in either a venting or an explosion of the cell.

A slow build up of methane in the cell can also result in a thermal runaway if the methane is ignited. Sources of the ignition can be hot spots or sparks within the cell resulting from shorts or high current discharges. Once the methane or other combustible gas is ignited the rapid increase in cell temperature and pressure can produce the same results as stated above.

A number of studies (16,17,19) have identified the ratio of Li/SO_2 as a critical factor in the safety of Li/SO_2 cells on forced overdischarge. Dey reported (19) that Li limited designs are the safest during overdischarge. In cathode limited designs he identified two conditions which appear necessary to produce an explosion on forced overdischarge: (i) occurrence of electrochemical reactions below zero volts resulting in the formation of active materials such as Li on the cathode and (ii) subsequent deep reversal corresponding to a so-called "trigger point" for explosion. The deep reversal corresponds to the polarization of the anode to potentials >2 volts. According to Dey, anode polarization in cells can occur either due to consumption and/or disconnection of the Li anode.

Since in all cases of explosion reported by Dey, the anode potential had risen to >2 volts, it is possible that sensitive materials were produced by oxidation reactions at the anode and "triggered" an explosive reaction in the cell.

One explanation for the irreproducibility of some safety incidents is the presence of impurities in individual cells. One common contaminant is water which can be introduced into a cell during the manufacturing process. The presence of an impurity such as water can affect the behavior of the cell by altering the protective $\text{Li}_2\text{S}_2\text{O}_4$ layer on the lithium, by causing the decomposition of products such as $\text{Li}_2\text{S}_2\text{O}_4$, or by catalyzing undesired exothermic reactions in the cell (12,46).

A thermal study by Dey (22) showed that the presence of moisture in a discharged cathode enhanced the decomposition of " $\text{Li}_2\text{S}_2\text{O}_4$ " and increased the caloric output by nearly a factor of ten. Results such as this show that it is necessary to consider the possibility that many of the irreproducible safety incidents were caused by unknown impurities in the cells.

A number of cells have exploded or vented upon being warmed after a discharge at low temperatures. In these cells it is likely that Li had deposited on the cathode due to inefficient SO_2 utilization and forced overdischarge. At low temperatures the reaction between Li and acetonitrile is slow. Thus as long as the cell is cold the Li does not react. However, as the cell is warmed the rate of the Li and acetonitrile reaction increases. If enough Li is present in the cathode the heat generated can be sufficient to create a thermal runaway situation within the cell. The result is the venting or explosion of the cell. It is most likely this mechanism that was responsible for the explosions reported in the NASA test (see safety incidents (viii) and (ix)).

The explosions experienced at NSWC by Frank Biss (safety incidents (x) and (xi)) are believed to have resulted from the ignition of methane which formed in the cells. It was suggested that upon discharging Li/ SO_2 cells the protective $\text{Li}_2\text{S}_2\text{O}_4$ layer on the anode is destroyed allowing the fresh Li to react with the acetonitrile before it is again passivated by SO_2 . When the cell is pulsed or shorted after a long stand time a spark or localized heating ignites the methane causing runaway reactions and cell venting.

A number of incidences (safety incidents xii-xv) suggest that discharged cells may contain shock sensitive materials. Lithium intercalation compounds with carbon have been shown to be potentially shock sensitive (42-45) thus their formation in Li/ SO_2 cells could account for some of the explosions reported.

It has also been shown that Li and Teflon react explosively when subjected to even mild shock (12,45). Since it is known that Li can be deposited onto the Teflon bonded carbon cathode this reaction is also probable.

It has also been speculated that species such as CH_3NC which could form at the anode during voltage reversal may be shock sensitive, particularly in the presence of Li (27,48,49).

On overcharge, Br_2 will probably be generated at the positive, although there are several reports that the SO_2 electrode is rechargeable (20,26), and $\text{Li}_2\text{S}_2\text{O}_4$ may be oxidizable to highly reactive sulfur-oxygen-containing species, for example, peroxymono- and di-sulfates. SO_2 could be oxidized to SO_3 which, in combination with AN, may be highly reactive. Bromine can react with Li, or the solvent, or other cell components. All of these potential reactions are very energetic. For example, we have observed that Al, initially at room temperature, will melt (m.p. 659°C) when exposed to 50% Br_2 in an AlBr_3 eutectic. On the other hand, our experience with Li plated from LiBr in PC or methyl acetate (MA) containing 1M Br_2 is that reaction takes place slowly at rates $< 1 \text{ mA/cm}^2$ and not at all explosively. In part, the reason that Al reaches a higher temperature

in contact with Br_2 than does Li is thermodynamic: the heat of formation of AlBr_3 is 126.0 kcal/mole vs. 85.7 kcal/mole for LiBr (50). No doubt too the reaction rate of Li is kinetically retarded, due to film formation. Under some cell conditions, the Li may not have time to film, and the Li- Br_2 reaction would become very fast.

Taylor and MacDonald (20) believe that the difference between charging fully discharged (which exploded) and fully charged cells (which did not explode) is at the negative. Specifically, in the former case much more fresh Li will be plated.

Another area of concern over the use of Li/SO_2 cells is the development of safe, environmentally acceptable methods of disposal of used Li/SO_2 cells. Unlike most other conventional cells the Li/SO_2 cell contains a substantial quantity of highly energetic, potentially hazardous materials at the end of its useful life.

Three (51,52) broad areas of concern which have been identified in recent studies of this problem are: (1) release of toxic or hazardous compounds (particularly cyanide) to leachate water; (2) release of toxic gases; and (3) fire or explosion hazard. As the use of Li/SO_2 cells increase the demand for an acceptable, economical disposal method will also increase.

4. SUMMARY

The safety of the Li/SO₂ cell has been greatly improved since its development early in the 1970's. The replacement of the crimped sealed cell with a cell containing a hermetic seal and an integral safety vent has minimized the leakage of SO₂ and reduced the overall safety hazard.

The major chemical attempt at reducing the instability of the Li/SO₂ system has been to achieve the correct balance between the capacity of the Li, SO₂ and cathode in order to maintain the cell in a stable condition at the end of discharge.

Despite the improvements, there are still many concerns about the safety of the Li/SO₂ system. The mere fact that the venting of a cell poses a serious safety hazard due to the release of toxic gases and possible flames requires that precautions be taken when using the cells.

The three areas of Li/SO₂ safety which need immediate further investigation are overdischarge, storage after partial discharge and low temperature discharge.

Overdischarge of Li/SO₂ cells was identified as the most frequent cause of a cell battery venting or exploding. Clearly this abuse mode needs to be examined to determine the underlying causes.

The susceptibility of Li/SO₂ cells and batteries to abuse after partial discharge and storage appears to be particularly hazardous in practical situations.

Low temperature discharge, particularly when a cell is driven into voltage reversal, appears to be another use where one can expect unsafe behavior of the Li/SO₂ cells. The cause of this problem appears to be the reaction of Li and acetonitrile, however, methods must be devised to prevent the reaction.

The future of Li/SO₂ cells depends on solving the safety problems experienced to date without creating new ones.

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